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16. ABSTRACT

Acid precipitation is a significant air pollution problem in North America and Europe. Here, large amounts of sulfur and nitrogen oxides and many other substances are emitted into the atmosphere from the combustion of fossil fuels, the smelting of sulfide metal ores, and other industrial processes. These oxides of sulfur and nitrogen are transported by wind over short and long distances and are transformed into a variety of substances that include sulfuric, nitric, and hydrochloric acids. These substances return to the surface of the earth in the form of acidic gases, aerosols, and precipitation. The resulting wet and dry deposition of acids and other chemical substances from the atmosphere is having a variety of effects on vegetation, soils, and surface waters. These effects are of interest to plant pathologists and physiologists, soil scientists and aquatic biologists, as well as to meteorologists and chemical climatologists in many regions of the world.

The purpose of this chapter is to review and evaluate the present state of scientific knowledge about the known and possible effects of acidic substances from the atmosphere on plants. Information from the peer-reviewed literature will be used exclusively in this review. The effects of other biotic or abiotic stress factors on plants will be considered only when these factors have a demonstrated interaction with acid deposition.

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ACIDIC PRECIPITATION EFFECTS ON TERRESTRIAL VEGETATION[1]

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Introduction

Acid precipitation is a significant air pollution problem in North America and Europe (29). Here, large amounts of sulfur and nitrogen oxides and many other substances are emitted into the atmosphere from the combustion of fossil fuels, the smelting of sulfide metal ores, and other industrial processes. These oxides of sulfur and nitrogen are transported by wind over short and long distances and are transformed into a variety of substances that include sulfuric, nitric, and hydrochloric acids (62, 77, 88, 126). These substances return to the surface of the earth in the form of acidic gases, aerosols, and precipitation. The resulting wet and dry deposition of acids and other chemical substances from the atmosphere is having a variety of effects on vegetation, soils, and surface waters. These effects are of interest to plant pathologists and physiologists, soil scientists, and aquatic biologists, as well as to meteorologists and chemical climatologists in many regions of the world.

The purpose of this chapter is to review and evaluate the present state of scientific knowledge about the known and possible effects of acidic substances from the atmosphere on plants. Information from the peer-reviewed literature will be used exclusively in this review. The effects of other biotic or abiotic stress factors on plants will be considered only when these factors have a demonstrated interaction with acid deposition.

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The Nature and Origin of The Acidic Substances in Wet and Dry Deposition

Chemical substances in the atmosphere include a wide range of organic and inorganic sustanaces that occur as gases, fine aerosol and coarse dust particles, and dissolved and suspended materials in cloud droplets and precipitation. These substances are removed from the atmosphere and transferred to the surfaces of vegetation and soils by dry and wet deposition processes. Dry deposition occurs continuously in all seasons of the year. It includes absorption and adsorption of gases and the impaction or gravitational settling of fine aerosol and coarse dust particles (6). Wet deposition occurs intermittently during rain, snow, and other precipitation events, which take place about 5% of the time in the humid regions of North America and Europe. Wet deposition includes the transfer of dissolved and suspended materials in raindrops, snowflakes, hail, dew, fog, and such special precipitation events as the formation of rime ice and the interception of cloud particles at high altitudes.

Many chemical substances in air and precipitation come from natural sources that include volatile emissions from the decomposition of plant and animal residues; wind-blown dust from desert regions and volcanoes, sea spray from oceans and large lakes; biogenic particles such as spores, pollen, and bacterial cells; smoke and soot particles from wild fires; and chemical transformations induced by lightning, solar radiation, and other chemical and physical forces in the atmosphere. Many chemical substances in air and precipitation also come from human activities (45). These include the combustion of fossil fuels; the smelting of metal ores; the controlled burning of agricultural and forest residues; the evaporation of volatile organic substances such as pesticides, liquid and gaseous fuels and industrial solvents; the decomposition or incineration of industrial, agricultural, or municipal waste materials, and the use of explosive devices in peace and war. Since the time of the industrial revolution, human activities have become progressively more important in determining the chemical climate of the industrial regions of the world (87).

The acidic substances in air and precipitation occur mainly in the form of acidic anions: sulfate, nitrate, chloride, carbonate, and bicarbonate. If the amounts of these acidic anions are balanced by equivalent amounts of alkaline earth or other cations, such as calcium, potassium, sodium, or ammonium, the dry or wet deposition from the atmosphere will be neither acidic nor alkaline. If the alkaline earth or other cations dominate, the wet or dry deposition will be alkaline. If the acidic anions dominate, the dry or wet deposition will be acidic.

In remote regions today and in the preindustrial periods of the world, wet and dry deposition is slightly acidic because the amounts of carbonate and bicarbonate slightly exceeds the amounts of alkaline cations present. Thus, the average pH of precipitation ranges from about 5.0–6.5 in the oceans and

other nonindustrial regions of the world. In industrial regions, however, where the combustion of fossil fuels and smelting of metals ores has been abundant, the balance between acidic anions (mainly sulfate, nitrate, and chloride) and acid neutralizing cations such as calcium, potassium, and ammonium has shifted, so that the average pH of precipitation is commonly in the range of 4.0–5.0, with individual precipitation events and dry deposition periods in the range between 3.0–4.0 and very occasionally even below pH 3.0. In certain regions of the world, where the sulfur and nitrogen emissions have been high and the acid neutralizing capacity in soils and bedrock has been low, the acidification of surface waters has resulted.

The purpose of this paper is to review and evaluate the impact that such acidity has or may have on vegetation.

Regional Variation in the Acidity of Wet and Dry Deposition

The chemical composition of rainfall in various geographic regions has been determined (43, 76, 110). Moreover, various estimates of amounts of SO_2 and sulfate deposited on terrestrial ecosystems have been made. One estimate is that 200 teragrams (tg) (1 tg = 10^{12} g) of sulfur move from the earth's surface to the atmosphere and back again annually. About 15 tg are absorbed by vegetation directly as SO_2, while about 20 (10%) and 80 (40%) tg are deposited as sulfates on terrestrial ecosystems by dry and wet deposition respectively (70). A similar estimate of annual sulfur deposition was obtained independently (42). A significant portion of this sulfur impacts upon land areas of the Northern Hemisphere. About 93% of all anthropogenic sulfur production occurs in the Northern Hemisphere and 80% of this total is deposited on land surfaces in that hemisphere (42).

Dry deposition constitutes about half of all sulfur compounds and these compounds may have some phytotoxic effects at high concentrations. The other major contributor of atmospheric sulfur deposition is wet deposition. Indeed, most of this sulfur is in the form of sulfate with associated H^+ and NH_4^+ ions (88). Wet deposition can be rain, snow, or fog. Although fog may constitute a significant portion of wet deposition in some areas, it usually does not result in large amounts of moisture input to foliage in most areas of the world. There are no estimates of the total amount of acidity deposited as dew or fog on vegetation.

Data from the National Atmospheric Deposition Program (NADP) for 1978 and 1979 show that the median pH of precipitation in portions of New York, Ohio, and Pennsylvania is less than 4.2, while most of the northeastern portion of the United States has a median below pH 4.4 (86). The pH levels derived from NADP are in good agreement with data from the Multistate Atmospheric

Power Production Pollution Study (MAP3S) and Electric Power Research Institute (EPRI) networks (92).

Currently, the acidity in precipitation events is categorized by the percentage of rainfalls within various pH ranges. Rain samples collected at MAP3S stations at Ithaca, New York, University Park, Pennsylvania, and Charlottesville, Virginia, were chosen for this categorization because they are three representative areas within the northeastern United States. Data for three years (1976–1979) are illustrated (29). Most rainfalls had pH levels between 3.5 and 4.5. Thirty-two percent of all rainfall samples had a pH below 4.0. Less than 0.5% of all rainfalls were below pH 3.0 or above pH 5.5.

Data from these national precipitation chemistry programs are derived from precipitation collectors that collect wet precipitation over periods of days, weeks, and months. Recent results suggest that most ambient rainfalls during the summer period of 1982 at an agricultural field site at Brookhaven National Laboratory, Upton, New York, were of short duration and were of low precipitation rate. Thirty-six events (33%) of the total had durations of less than 2 minutes and 47 events (43%) were less than 10 minutes long. Forty-two events (38%) were between 11 and 140 minutes, while the remaining 19 were more than 140 minutes. A majority of events had rates less than 1.5 mm hr^{-1} and only 12.5% of all events had rates greater than 3.5 mm hr^{-1}. Over 50% of all ambient showers during the summer period had volumes below 0.25 mm. Moreover, only 8% of all events had amounts greater than 8 mm (33). These data indicate that the majority of all ambient rainfall events at Brookhaven in 1982 were of relatively short duration and small volume (31, 32).

These data that document many small-volume, short rainfalls do not take into account the frequency and duration of dew on vegetation surfaces. During the 1979 growing season at Upton, New York, it was determined that dew conditions were present for more than 2 hours 65 times (a total of 755 hours) (31). Moreover, dew conditions were present for more than 2 hours 36 times for a total of 226 hours during the 1981 growing season at the same site (34). All these data taken together suggest that foliage is wetted numerous times during the growing season and that information about the chemistry of these short-duration, low-volume rainfalls and dew may be obscured by the chemistry of longer-duration, larger-volume precipitation samples.

Most high-acidity values in rainwater in the eastern US were found in the spring and summer (97). The mean (weighted) hydrogen ion concentration in rainfalls at Brookhaven National Laboratory was almost 10^{-4} M (pH 4.0) during the summer of 1977. Values for spring were about 4.5×10^{-5} M (pH 4.35) and the mean concentrations for winter and fall were similar at about 2.3×10^{-5} M (pH 4.64). These observations indicate that rainfall acidity is highest during the growing season.

Interaction of Precipitation and Leaf Surfaces

In theory, the amount of injury to plant foliage by acidic precipitation depends upon the area of leaves in contact with rainwater. Moreover, injury may also depend upon the rate of absorption of materials from rainwater per unit area. The amount of water absorbed by foliage depends upon many characteristics, the waxiness of the leaf surface or the number of cuticular pores, for example. These characteristics vary among plant species and, as a result, may determine relative species sensitivity to precipitation acidity.

The amount of foliar injury probably is a function of the degree of foliage wettability. The attraction of a liquid to a solid surface upon impaction is an important measure of the amount of water retained on the surface. However, the area over which a droplet spreads depends upon the relative amount of attraction between the liquid and the surface. The advancing contact angle has been used as the criterion of leaf surface wettability (83) and is defined as the angle between the surface of the leaf and the tangent plane of a water droplet at the circle of contact between air, liquid, and leaf. A zero-degree angle maximizes wettability, while an angle of 180° provides virtually no wetting. Contact angles of pure water drops may be as small as 31° on *Phragmites communis* or greater than 150° on *Triticum aestivum* and *Lupinus albus* (51, 68, 80). In this way, the contact angle is determined mostly by the chemical and physical characteristics of epicuticular waxes and to a lesser extent by surface roughness (83). Wettability of leaf surfaces increases markedly when the cuticle and epicuticular waxes are removed (38).

Solutions must penetrate through cuticle layers or through stomata to reach leaf cells. It has been postulated that cuticles are perforated by micropores (16). Cuticular pores may be numerous in specialized areas, such as at bases of trichomes, hydathodes, glandular hairs (106), water-absorbing scales of *Bromeliaceae* (50), and stigma tips (71). Although cuticular pores may not be present (83), solutions penetrate faster at these locations. This may explain why injury from acidic precipitation occurs more frequently at these sites (see below). Penetration of rain or leaf-surface solutions through stomata is thought to be infrequent, if it occurs at all (4, 48, 49, 102). Generally, spontaneous water infiltration of stomata will occur if the contact angle is smaller than the wall angle of the aperture wall. The degree of stomatal opening from 4 to 10 μm is of little importance in water penetration. However, cuticular ledges present at the entrance to the outer vestibule and between the inner vestibule and substomatal chamber result in very small wall angles. The latter situation plays a major role in excluding water from stomata (108). In this way, the main route of entry of absorption of substances from precipitation should be through the cuticle.

In theory, non-polar molecules should penetrate the cuticle at rates faster than those of polar molecules because of the non-polar nature of both cutin and epicuticular waxes of the cuticle (89). More polar compounds, such as inorganic ions and water, may preferentially enter the leaf via pectinaceous channels that traverse the cuticle (101). It is postulated that the ratio of cutin to wax in the cuticle greatly influences the degree of penetration of polar substances (83).

Solution acidity may also affect cuticular penetration rates (107, 109). In experiments with isolated apricot leaf cuticles, rates of penetration of acidic substances increased with an increase in solution acidity. The rate of penetration of basic substances increased with a decrease in solution acidity. These relationships between pH and sorption rates with apricot cuticles (91) have been verified with isolated cuticles (84) and intact bean leaves exposed to buffered solutions (25).

Cuticles and epicuticular waxes should not be considered inert, non-differential barriers to ion permeability. Relative permeability coefficients of isolated cuticles to various mono- and divalent cations differ by as much as a factor of 6.

The idea of differential or selective uptake of chemical constituents by foliage is reinforced by other experimental data. Penetration of chemicals into foliage is affected by both metabolic and non-metabolic processes. Reversible diffusion through cuticles is followed by metabolically controlled uptake through cellular membranes (94). There are many examples of light-enhanced foliar uptake (9, 48, 103) being retarded by inhibitors of protein synthesis (69). In this way, uptake of various elements by foliage is selective to an unknown degree and is dependent upon the metabolism of leaf cells.

Some regions of the cuticle are more permeable than others. For example, basal portions of trichomes (60) and guard cells (19, 102) are preferential sites of absorption. Moreover, absorption of water-soluble materials may be rapid through the cuticle near veins (75, 80). These studies are germane because about 95% of all foliar lesions following exposure to simulated acidic rain occur near bases of trichomes, at guard and subsidiary cells of stomata, and along veins (24, 26–28). Recently, these results have been confirmed with other species (3, 93). From these data it seems reasonable to conclude that phytotoxic components of simulated acidic precipitation penetrate the cuticle with greater frequency and faster rates in specific areas.

Acidic precipitation may change the surface characteristics of foliage. It has been suggested that acidic precipitation may affect the submicroscopic structure of the epicuticular wax layer(s) of leaves. Shriner (113) showed that leaves of kidney bean and willow oak exposed to simulated rain of pH 3.2 had lost superficial waxes, cutin, and cuticular waxes. There was only slight erosion on leaves exposed to simulated rain of pH 6.0. In contrast, Paparozzi (93) showed no erosion of epicuticular waxes or cuticular waxes on either yellow birch or

kidney bean after exposure to simulated rainfalls as low as pH 2.8. The cuticular waxes were not structurally changed by simulated acidic rain, even though underlying cells were affected. Moreover, it should be noted that the most widely used methods of isolating cuticles involve exposure to strong acids (59, 84). Since strong acids are used to isolate intact, functional cuticles, it may be inferred that acids at concentrations present in current ambient rains do not damage cuticles. Penetration rates of elements through isolated cuticles were similar to rates through intact cuticles in situ (25). At the present time, a relationship between changes in the cuticle, including cutin and epicuticular waxes, and changes in leaf cells remains to be established.

Leaf surfaces may also change the chemistry of rain solutions. The acidity of rainwater may be changed by chemicals from leaves as raindrops dry. Adams (3) demonstrated that leaves of several plant species have differing buffering capacities. The pH of simulated raindrops (50 μl) of pH 5.6, 3.5, and 3.0 usually increased during the 75-minute time periods measured. However, when the initial pH was 2.5 the pH always decreased as time passed. The pH of a parafilm surface (control) was always lower than that of any of the plant surfaces, suggesting that the leaves produced substances to neutralize the acidity. The presence of substances on leaf surfaces produced by leaves has been recognized for almost a century (122). Recent results from our laboratory substantiate the results of Adams (3). In our studies the differences between pH changes on bean leaves not exposed to any solutions and teflon plates (controls) were not as marked as the differences documented by Adams (3), although the test solutions were very similar.

Inputs of Materials into Foliage

A wide variety of chemicals are found in ambient rain (44, 78, 79, 99). It is of interest to understand if materials in rain can be absorbed by foliage and if rainfalls can remove materials from foliage. Recent information suggests that materials can be absorbed at differing rates from rainfalls of varying acidity (25). For example, sulfate penetrated leaves faster at pH 2.7 than at 5.7, while $^{86}Rb+$ penetrated faster at pH 5.7 than at lower pH levels. Tritiated water entered foliage at similar rates at all pH levels tested. In addition to differences in uptake due to acidity, rates of incorporation of various ions may vary markedly. Water penetrated leaves much faster than $^{86}Rb+$, followed by sulfate ions. Water molecules entered foliage about one thousand times faster than did sulfate ions (25). These results suggest that absorption of materials in water on leaf surfaces is a selective process that may be affected by solution acidity. However, individual ions appear to have their own specific entry rates that may be affected by many intrinsic and extrinsic factors.

Foliar fertilization may occur by means of inputs of nitrogen and sulfur from ambient rainfalls. Little information is available to evaluate the amount of

incorporation into foliage of nutrients in rain. The rate of entry of sulfate is a low percentage of the amount in solution (25). The only other information about the incorporation of nitrogen and sulfur into foliage from solutions may be derived from foliar fertilization experiments. Of course, the application of fertilizers on foliage is usually performed with surfactants, not present in ambient rain, to enhance uptake.

Increases in soybean seed yields result when large quantities of N (80 k/ha), P (8 kg/ha), K (24 kg/ha), and S (4 kg/ha) are applied to foliage of soybeans during pod filling only (46). From available evidence the optimum NPKS proportions in the fertilizer solutions for soybeans should be 10:1:3:0.5. Inconsistent results occurred with other combinations so that many other nutrient combinations, even with high nitrogen (24 kg/ha^{-1}) and sulfur (12 kg/ha^{-1}) applications, resulted in no-yield effects (46).

Throughout the growing season of 1981 in Upton, a total of 18.1 kg N ha^{-1} as nitrate and 102 kg S ha^{-1} as sulfate were supplied in simulated rainfalls at pH 2.7 and no obvious growth stimulation occurred (34). These rather high inputs of N and S can be compared to the relatively low (1.80 kg N and 2.73 kg S per hectare) amounts applied by ambient rainfalls during the same time period. There are no experimental data that document foliar fertilization of any plant species at N or S concentrations present in ambient rain.

Characteristics of Visible Foliar Injury

Simulated acidic rain–induced lesions on vegetation occur mostly on leaves and reproductive structures (24–27, 47, 67). Simulated rain at about pH 3.4 is the highest pH at which visible lesions on leaves have been observed. A significant percentage of the leaf area may exhibit lesions. For example, about 0.5%, 2–3%, 5–10%, and 10–15% of the leaf area of pinto beans is injured after one to four exposures to simulated acidic rain at pH levels of 3.0, 2.7, 2.5, and 2.3 respectively (26). In this way the area showing injury increases with an increase in rainfall acidity.

Visible leaf injury is most pronounced on foliage of some species just prior to full leaf expansion (21, 22, 24, 26, 27). Densities of trichomes and stomata per unit leaf area are highest in young leaves and lowest in fully expanded leaves. Since the amount of visible leaf injury does not coincide with the density of either stomata or trichomes at full leaf expansion, other factors such as surface wettability must be involved in predisposing leaves to injury. Wood & Bormann (124) suggest that young (14 day–old) birch seedlings are much more sensitive than older (six weeks old) seedlings, while Paparozzi (93) showed that mature leaves are as susceptible to foliar injury as enlarging birch leaves. Needle elongation is inhibited if simulated acidic rain solutions are applied to immature pine fascicles (47, 55).

Leaves of several plant species have reacted to exposure to simulated acid

precipitation by producing galls (26, 27). Water from subsequent rainfalls did not pool in these elevated locations, so less injury (total area) resulted. Galls were produced by abnormal cell proliferation (hyperplasia) and abnormal cell enlargement (hypertrophy). These results have been confirmed on *Artemisia tilesii*, pinto beans, and spinach (3). In this manner, the hyperplastic and hypertrophic responses of foliage may alleviate extensive foliar injury. These responses may be related to the lower amounts of visible foliar injury in these species.

At the present time there is only one documented occurrence of visible foliar injury attributed to ambient rainfalls (32). Visible foliar injury, identical to that caused by simulated acidic rainfalls of pH 4.0 and below, was produced on foliage of field-grown garden beets during a three-day period in which three short-duration, low-volume rain showers with pH levels of about 3.8–3.9 occurred. Simulated rainfalls of higher acidity resulted in lower beet yields, which were attributed to both a smaller number of saleable roots per plot and a lower fresh mass per saleable root.

Experiments were performed to determine the relative sensitivity of various species to simulated acidic rain. Based upon visible effects on foliage, it has been suggested that sensitivity ranks from high to low in the following order: herbaceous dicots, woody dicots, monocots, and conifers (21, 24). Within each species, the amount of visible leaf injury appeared to relate linearly to the hydrogen ion concentration of the simulated rain solution (22).

Leaching of Materials from Foliage

Since plants produce substances on their surfaces, it is of interest to determine if removal of these substances is influenced by the acidity of precipitation. Moreover, substances within leaves may be released after exposure to rainfalls, and the nutrient levels in harvested portions of crops may affect the quality of foodstuffs. It is conceivable that precipitation acidity could influence nutrient leaching from plant surfaces sufficiently to alter crop quality. Wood & Bormann (125) demonstrated that K^+, Ca^{2+}, and Mg^{2+} were leached from pinto bean leaves more rapidly at pH levels of 3.0 and 3.3 than at pH levels of 4.0 and 5.0. Ca^{2+} leached faster at pH 3.0 than at pH 3.3 from foliage of sugar maple. Leaching rates of K^+ and Mg^{2+} were higher at pH 3.0 than at pH 4.0. In tobacco leaves, Ca^{2+} leached faster from foliage exposed to simulated rainfalls of pH 3.0 than from foliage exposed to pH 6.7 (36). In pinto beans exposed to a 20-minute daily treatment of simulated rain for five days, more calcium, nitrate, and sulfate were leached from foliage at pH levels of 2.7, 2.9, and 3.1 than plants exposed to 5.7 (25). In contrast, the amount of potassium leached was greater from leaves exposed to pH 5.7 than from leaves exposed to pH levels between 3.4 and 2.9. The amounts of ammonium, magnesium, and zinc were the same at all pH levels tested. Detectable quantities of three radioiso-

topes were detected from leachates from leaflets of *Phaseolus vulgaris* that were exposed to one 20-minute simulated rainfall 24 hours after radioisotope addition. Although the quantities $^{3}H_2O$, $^{86}Rb^{+}$, and $^{35}SO_4=$ were less than 1% of the radioisotopes in leaflets, these results demonstrate that recently absorbed ions may be leached by rainfall.

Cole & Johnson (15) measured pH and conductivity, a measure of the total cations and anions present, of ambient precipitation and throughfall during two rainfalls in 1973. During the latter portion of the first rainfall, the pH of the throughfall (≈4.0) was about 1 pH unit below that of ambient precipitation (≈5.0). Conductivities of the two solutions were similar at about 10 micromhos per centimeter. During the second rainfall, the pH of ambient precipitation (≈3.5) was almost 2 units below that of the throughfall (≈5.3). Over an entire annual cycle, the amount of sulfur in throughfall was greater than in ambient precipitation. Cole & Johnson (15) concluded that the differences in sulfur content observed were due to foliar leaching. Moreover, van Breemen et al (123) demonstrated that ammonium, nitrate, and sulfate volume-weighed concentrations are higher in throughfall and stemflow than ambient rain from forests at two locations in the Netherlands. These results suggest that N and S may be leached from trees when exposed to rainfalls of pH 4.29 and 4.51. However, washoff of dry deposition may also have contributed to higher sulfate concentrations in throughfall. At the present time there are no data documenting significant foliar leaching of materials at present levels of precipitation acidity that could produce changes in plant growth or productivity.

Influence on Foliar Gas Exchange

Several years ago it was proposed that acidic precipitation might affect the rate of gas exchange by stomata (118), and that epidermal cells may be injured preferentially upon initial exposure to acidic rain (52, 54). Since guard cells are preferentially affected, it was postulated that acidic precipitation might affect gas exchange rates. In *Phaseolus vulgaris* diffusion resistance was much lower in foliage exposed to simulated rain of pH 2.7–3.4 compared with foliage exposed to rain of pH 5.7 (25). These results suggest that foliage exposed to acidic rain may be more subject to wilting or water stress. Moreover, such foliage may be more sensitive to exposures of gaseous air pollutants. This decrease in resistance may also increase carbon dioxide uptake for photosynthesis. Knowledge of the effects of rainfall acidity in combination with gaseous pollutants such as ozone and sulfur dioxide is needed in order to understand the total impact acidic rain might have on vegetation.

Influence on Cell Metabolism

Although the cell cytoplasm has a large buffering capacity (119), small localizations of protons reacting with membranes could at least modify membrane

function in terms of electron or proton gradient pumps necessary for intracellular energy production even if they do not alter membrane permeability and/or integrity. Subtle alterations in membrane function could alter the energy relations of cells (82). Specifically, a slight change in the proton concentration across a membrane may disrupt the production of ATP by cells as forwarded by the chemiosmotic theory of energy production (57). Of course, disruption of the plasmalemma would produce rapid cell necrosis. The actual mechanism(s) by which protons on foliage have phytotoxic effects at the cellular level is (are) unknown.

The metabolic conversions of both sulfate and nitrate (major anions in acidic precipitation) in plants are known in some detail (53, 54, 105). Both sulfur and nitrogen are essential elements of plant nutrition. Small quantities of sulfate and nitrate applied to foliage might be incorporated into molecules such as proteins that are vital to cells (see above). From available evidence it seems unlikely that the present sulfate and nitrate concentrations in ambient rainfalls could be phytotoxic.

Alterations in Photosynthesis and Respiration

Photosynthesis and respiration measurements were made using leaves of *Phaseolus vulgaris* after exposure to simulated acid rain (37). Extensive lesions occurred on leaves after exposure to pH levels of 2.0 and 2.5 compared with exposure to pH 5.5. Although rates of respiration and photosynthesis were higher in leaves exposed to acidic solutions than in control leaves, net photosynthetic rates (photosynthesis minus respiration) were similar at all rainfall pH levels tested when results were compared on a fresh weight basis. These results suggested that there might be no change in carbohydrate production among the treatments. However, leaves exposed to simulated acidic rain (pH 2.3) had lower sugar and starch contents compared with plants exposed to simulated rain of pH 5.7. Foliage exposed to acidic rain may be stressed, but short-term measurements of photosynthesis and respiration may not be sensitive enough to detect the degree of stress.

Seed Germination and Seedling Emergence

Lee & Weber (74) exposed seedlings of eleven woody species to simulated rainfalls (23 mm weekly) of pH 3.0, 3.5, 4.0, and 5.6 for time periods up to 9 months. Seedling emergence of eastern white pine (*Pinus strobus* L.), yellow birch (*Betula alleghaniensis*, Britton), eastern red cedar (*Juniperus virginiana* L.) and Douglas fir (*Pseudosuga menziesii* var. menziesii, Franco) was significantly greater with high acidity rainfalls compared with controls. In contrast, emergence was lower for Staghorn sumac (*Rhus typhina* L.) under acidic rain exposure compared with controls. No significant treatment effects were detected for 7 other species tested. In similar experiments by Raynal et al

(96), seedling emergence in yellow birch and red maple was inhibited at low pH levels compared with controls, while emergence of white pine was highest after exposure to simulated acidic rain. No significant treatment effects were present for sugar maple. Moreover, Baldwin (8) found better germination of red spruce under more acidic conditions. From available data, it seems that seedling germination and emergence can occur over a wide range of substrate levels. At present, it is not possible to evaluate the ecological significance of acidic rain treatment effects as they relate to natural systems.

Crop Growth and Yields (Controlled Environments)

Reductions (19% and 11%) in dry weight of trifoliate leaves and dry weights of pods and seeds, respectively, of bush beans occurred after exposure to acidic mists (pH 3.0) with no visible leaf injury (56). In contrast, Wood & Bormann (124) showed that simulated acidic mists of pH 3.0 did not reduce growth rates of yellow birch even though all leaves exhibited some leaf pitting and curling. However, crop yields may be determined by development and survival of reproductive organs as well as by cumulative injuries to foliage. No consistent relationship between the amount of visible foliar injury and the amount of seed yield has been demonstrated among various plant species exposed to acidic precipitation.

Lee et al (73) conducted experiments with 28 crops grown in pots in field chambers. Simulated acidic rain was applied at pH levels of 5.6, 4.0, 3.5, and 3.0. The lower pH rains gave smaller marketable yields in five of the 28 crops tested (radish, beet, carrot, mustard greens, and broccoli) and larger yields in six crops (tomato, green pepper, strawberry, alfalfa, orchard grass, and timothy). No consistent effects were observed for sixteen other crops. The experimental results suggest that the probability of yield being affected by acidic rain depends upon the plant species as well as the part of the plant utilized. Foliar injury was not always related to effects on crop yields.

In recent experiments, simulated acidic rain of pH 3.1 and below decreased dry mass of seeds, leaves, and stems of pinto bean plants exposed to 45 20-minute rainfalls throughout the growing season under greenhouse conditions (30). On a percentage mass basis the decrease in seed yield was comparable with reductions in biomass of leaves and stems. The decrease in yield of pinto beans by simulated acidic rain was attributed to both a decrease in the number of pods per plant and a decrease in the number of seeds per pod. In soybeans, application of 78 simulated acidic rainfalls decreased the dry mass of both stems and leaves. Seed yield also decreased after treatment with rain of pH 2.5. However, an increase in seed yield occurred when plants were exposed to rainfalls of pH 3.1. A larger dry mass per seed was responsible for the larger dry mass of seeds per plant exposed to simulated rainfalls of pH 3.1 (30).

Significant effects of rainfall acidity were not observed on apple seedlings

unless the pH was below 2.75 compared with controls (pH 5.6). Moreover, both leaf and seedling growth rates were not different between pH 7.0 and 2.75 when 14 plants per treatment were harvested after nine once weekly (amount of water applied not given) rainfalls (39). The pH levels of ambient rainfalls did not affect fruit quality or production in grapes or apples. However, reductions in pollen germination, fruit set, and fruit quality were observed below pH 3.1 for some cultivars (40, 41).

Crop Growth and Yield (Field Conditions)

Because root yields of radishes were reduced after exposure to simulated acidic rainfalls under controlled conditions (73), two experiments have been performed with field-grown radishes (32, 121). Troiano (121) exposed four plots per treatment and demonstrated a significantly higher root yield (dry mass) at high acidity rainfalls (13%) compared with simulated rain of pH 5.6. No statistically significant yield effects were demonstrated in an experiment that utilized 45 plots per treatment (32). It should be noted that roots from the first harvest in the former experiment (121) were 3–4 times greater than yields of the latter experiment (32) and from roots purchased from commercial markets.

Significant reductions in garden beet yields were obtained with plants receiving applications of simulated rainfalls in addition to ambient rainfalls. Plants exposed to simulated rainfalls of pH 4.0, 3.1, and 2.7 were 76%, 86%, and 85% of yields of plants exposed to rainfalls of pH 5.7 (32). No significant yield reductions were obtained for kidney beans and alfalfa.

Several field experiments have been performed with soybeans. In one experiment (Experiment 1) at Yonkers, New York, plants were grown in open top chambers (OTC), one treatment per chamber (63, 120). The experiment treatments were pH 4.0, 3.4, and 2.8. A clear plastic tarpaulin was loosely secured over the top of each chamber. Within the OTCs, light transmission was decreased up to 25% and temperatures were elevated up to 3° C above ambient conditions. Eighteen simulated rainfalls of 12.7 mm each for a duration of 60 minutes were applied over a period of 50 days during the latter portion of the growing season. These simulated rainfalls provided a mean of 4.6 mm of water daily.

A second experiment (Experiment 2) was performed in Kendall County, Illinois, in 1977 and 1978 (61). Experimental plots were placed at two different locations in the same field during the two-year study. Only one experimental plot (four 5-meter rows in 1977 and four 6-meter rows in 1978) per treatment was used each year. In both years, simulated rain and ambient rain treatment plots were also exposed to both ambient and artificially elevated concentrations of sulfur dioxide. The treatments were pH 5.25, 4.09 (ambient only), and 3.06 in 1978; they were 3.17 in 1977. Simulated rainfalls were distributed from a

single nozzle for each treatment plot, while sulfur dioxide was administered from a gas distribution system above the plant canopy.

Eight and eleven simulated rainfalls provided 3.38 and 4.46 cm of water in 1977 and 1978 respectively. These treatments provided 36% and 49% more water to experimental plots than the control plot, which received only 9.39 cm of water during the treatment period in 1978. Thus, not all plots received the same amount of water. Plants were exposed to eleven simulated rainfalls, 4.1 mm of water over a period of 20 minutes each, an average of 1.4 times weekly for 54 days during the second half of the growing season in 1978. The simulated rainfalls of pH 5.25 and 3.17 provided calculated mean weighted pH values of 4.25 and 3.47 compared with an ambient rainfall pH of 4.09.

A third experiment (Experiment 3) was performed at Upton, New York (34). Two simulated rainfalls of 12.7 mm each provided 25.4 mm of water weekly for 15 weeks. Each simulated rainfall occurred for 1.75 hours between 1800 and 2400 hours. The crop received no measurable water from ambient rain because it was shielded by covers. All treatments received the same amount of water. Four replicates of four treatments of simulated rainfalls of pH 5.6, 4.1, 3.3, and 2.7 were arranged in latin squares. The field-plot design included eight complete latin squares yielding a total of 32 plots per treatment with four rows per plot. In this experiment, plants were shielded from all ambient rainfalls by two 30 × 10 meter moveable rainfall exclusion shelters. All four rows of each plot were exposed to simulated rainfalls.

A fourth experiment (Experiment 4) was also performed at Upton, New York, during the summer of 1981 (34). Four replicates of four experimental treatments of simulated rainfalls of pH 5.6, 4.1, 3.3, and 2.7 were arranged into latin squares. The field plot design included eight latin squares yielding a total of 32 plots per treatment. These plants were not shielded from ambient rainfalls. The weighted mean acidities of all precipitation on plants exposed to ambient rain plus simulated rainfall treatments of pH 5.6, 4.1, 3.3, and 2.7 were equivalent to pH 4.07, 4.04, 3.92, and 3.64 respectively. Plants received three weekly exposures (between 0800 and 1200 hours) to simulated precipitation in sufficient quantities to wet the foliage only. These simulated rainfalls added only 16.7 mm more water than ambient rainfalls (211.6 mm) throughout the growing season. Each simulated rainfall provided water similar to the mode of all ambient rain showers (31, 32). This was sufficient to wet the foliage.

Different conclusions have been drawn from the results of these four individual experiments with field-grown soybeans. In Experiment 1 (63, 120), soybean seed yields were not significantly related to rainfall acidity in either filtered or unfiltered air. In Experiment 2 (61), simulated acidic precipitation also produced no statistically significant effect on seed yield. Decreases in soybean yields due to acidic precipitation were observed in Experiments 3 and 4 (33, 34). An analysis of variance of selected subsets of one, two, four, and

eight latin squares of Experiment 3 provides some insight on field variability (35). The eight latin squares analyzed as individual experiments (4 plots per treatment) yielded erratic results. Statistically significant linear comparisons were detected in four of the eight latin squares. When two randomly selected latin squares (8 plots per treatment) were used in the analysis of variance, the linear component was just significant at the 1% level. When four latin squares (16 plots per treatment) were used, the linear component was highly significant. When eight latin squares (32 plots per treatment) were combined, the evidence that the treatment differences may be attributed to a linear gradient is overwhelming. The low probability value for differences among latin squares indicates that field locations are a legitimate source of stratification. These results demonstrate that inadequate replication may result in a failure to detect both statistically and biologically significant differences.

The most important difference in these experiments is their statistical designs. Two of the field layouts (Experiments 1 and 2) (61, 63, 120) used only one plot per treatment. These provided no replication except in the sense of plants, rows, or sectors within the single plot. Such studies are subject to the criticism that treatment effects are necessarily confounded with plot effects. That is, treatment effects cannot be separated from other microenvironmental variables peculiar to a specific plot location. Experiments 3 and 4 (33, 34) were highly replicated. They were designed to detect differences of 10% or less among treatment means. Type 1 error, α, was predetermined, and replication was sufficient to keep Type 2 error low. This design was made possible because a preliminary experiment was available to estimate the expected components of variance. Despite differences in the procedures and protocols among the four experiments, it is primarily the quality of the experimental design that has determined their validity and relative utility for crop-loss assessment.

Effects of Acidity on Lower Plants, Bacteria, and Plant Pathogens

The above discussion has centered on the biological effects of acidity and sulfur compounds on foliage of higher plants. Most multicellular organisms that have evolved from aqueous environments onto dry land have evolved specialized surfaces to retard desiccation. Present evidence indicates that organisms with protective coverings are less sensitive to rainfall acidity than organisms that lack these coverings. For example, lichens, bacteria, and other single-celled organisms are very sensitive to pH changes. Procaryotic organisms survive within a smaller range of pH levels than most multicellular organisms (5, 90, 112). Motility of most procaryotic organisms is greatest between pH 6.8 and 9.0 (5, 90, 112). Motility has been used as a measure of survival in such organisms. A 50% decrease in the velocity of flagellar movement occurred in *Bacillus brevis* when the pH was reduced from 7.5 to 5.0. Heoninger (58)

showed that a pH decrease results in an increase in abnormal wave motions in flagella of *Proteus*. Below pH 5.0 almost all motility ceased.

Fertilization and spermatozoid motility in gametophytes of bracken fern are very sensitive to low pH and additions of sulfate, nitrate, and chloride (20). Spermatozoid motility at pH levels 6.0, 5.5, and 5.1 was about 70%, 50%, and 30% respectively of values obtained at pH 6.1 2–4 minutes after exposure. Motility at sulfate concentrations of 43.3, 86.6, and 173.2 μM at pH 6.1 was about 60%, 45% and 35% respectively of values obtained with no sulfate additions. Fertilization decreased as pH decreased below pH 6.1. Fertilization after a 3.5 hour exposure to pH 5.5, 5.1, and 4.5 was about 90%, 75%, and 60% respectively of values obtained at pH 6.1. Fertilization values at sulfate concentrations of 43.3, 86.6, and 173.2 μM at pH 6.1 were about 85%, 75%, and 60% respectively of values obtained with no sulfate additions (20). Similar results were obtained in field tests (23). Experimental results with bracken fern were similar to results of megaspore germination and sporophyte formation in the heterosporous fern *Marsilea vestita* (81). Germination of megaspores was much more sensitive to low pH than was sporophyte development.

Photosynthesis in the caribou lichen *Cladina stellaris* (Opiz) is affected by the chemistry of simulated rainfall solutions (72). When dried tissues were exposed to simulated rainfalls of pH 5.6, maximal rates of photosynthesis occurred in about 6 hours. Tissue wettings with low sulfate (0.53 mg l^{-1}) simulated rain of pH 4.0 resulted in photosynthesis rates 43% below controls 6 hours after wetting. Similar results were obtained at high sulfate concentrations (10.00 mg l^{-1}). Although such lichens are a major winter food resource for caribou and reindeer (10, 52) the overall impact(s) of the documented decreases in photosynthesis remains unknown.

Many microorganisms inhabit surfaces of higher plants. A particular microorganism may have a positive (beneficial), negative (pathogenic), or neutral influence upon normal plant growth, development, and reproduction (see reviews in 18, 95). Leaf surface bacteria within a canopy of Douglas fir may fix significant amounts of nitrogen (65). Many pathogenic bacteria and fungi infect aerial portions of plants. These pathogens can reduce crop yields substantially (100, 111). Effects of air pollutants on relationships between host plants and their leaf-surface microbes have been reviewed (116). An air pollutant may differentially influence host and microorganism. Many researchers have conducted experiments to detect interactions between hosts and microbes exposed to air pollutants (17, 104, 116). In similar tests with simulated acidic rain (pH 3.2), Shriner (114) found an 86% inhibition of telia number of *Cronartium fusiforme* on willow oak *(Quercus phellos)* compared with pH 6.0 under greenhouse conditions. He also found that halo blight caused by *Pseudomonas phaseolicola* on leaves of greenhouse grown *Phaseolus vulgaris* was stimulated or inhibited by simulated acidic rain, depending upon the stage of disease

development when rainfalls occurred. Simulated acidic rain inhibited initial infection of the pathogen but stimulated development of the pathogen after infection to increase injury to host.

In field experiments (114), kidney bean plants that received simulated rainfalls of pH 3.2 had 34% as many hematode egg masses per root system as plants that had received simulated rain of pH 6.0. All plants received ambient rainfalls in addition to simulated rainfalls. Plants that had received the low pH rainfalls had only 48% as much root surface galling as plants that received pH 6.0. Biomass of roots, shoots, and pods as well as soil pH were not significantly affected by the simulated rain treatments. Bean leaf area injury caused by bean rust *(Uromyces phaseoli)* was not consistently affected by simulated rainfall acidity under field conditions. There are no experimental field data that demonstrate that rainfall acidity effects host-pathogen relations that result in significant changes in plant productivity or survival.

Indirect Effects on Vegetation: Soil Effects

The actual and potential effects of acidic deposition on soils and the impacts of soil systems on freshwater chemical changes have been reviewed elsewhere (7, 29, 64, 85, 98). These reviews will provide a basis for an understanding of how changes in soil chemistry may impact upon terrestrial vegetation.

Legume-Rhizobium Interactions

Since acidic rainfalls may affect host-parasite relationships, rainfall acidity may affect legume-*Rhizobium* relationships. Numbers of nodules per plant was reduced when soybean and kidney bean plants were exposed to simulated rainfalls of pH 3.2 under either field or greenhouse conditions. The reduced number of nodules per plant did not result in decreased shoots, roots, or pods in most experiments (115). Nodulation of red clover and birdsfoot trefoil was also sensitive to simulated acidic rainfalls when plants were grown in soils from Panther Lake and Woods Lake watersheds of the Adirondack region of New York. Nodulation was not affected in one study where an agricultural soil was used (13). In all three soils, the dry mass and nitrogen contents of roots and tops were significantly lower from plants exposed to high acidity rainfalls compared with controls. These results are consistent with results of some field experiments with field-grown soybeans that show reduced seed yields and seed protein contents after exposure to high acidity rainfalls (31, 34).

Ecosystem Effects

Several field experiments have been conducted in forests. Perhaps the first field experiment to test for effects of acidic rain on forests began in 1969 (117). Sulfuric acid levels of 50, 100, and 150 g per hectare per year were added to

soils. Treatments usually included the presence and absence of supplemental irrigation and fertilization at 60, 120, and 180 g nitrogen per hectare per year, with and without acid additions. Although treatments of 100 g S as H_2SO_4 per hectare per year killed most of the ground vegetation such as mosses, lichens, and *Callum vulgaris*, there was no evidence of a negative effect on tree stem volume growth. From these results, Tamm (117) concluded that except in areas where forest trees exhibit visible pollution symptoms, ambient acidic precipitation and other types of atmospheric acidity probably have little or no effect on tree growth. However, it should be recognized that since only three plots per treatment (two plots per treatment in some experiments) were used, variations among plots could easily have overshadowed differences among treatments.

In contrast to the experiments of Tamm, other researchers in Sweden found a statistically significant difference in tree growth between areas exposed to acidity and areas more remote from transported atmospheric acidity (66, 67). They concluded that there was no reason to attribute the growth reduction to anything other than acidic rain. In contrast, researchers in Norway (2) and the United States (14) have not detected any consistent decreases in tree growth within forests. At present, the effects of precipitation acidity on forest productivity remain unknown. More recently, a forest growth simulation model (11) was used to estimate potential effects of acidic rain on forest ecosystems where only increases in foliar injury were considered. This model predicted that visible foliar injury of up to 5.5% of leaf area would produce no decreases in total forest productivity. The results imply that a reduction of leaf area of 10–25% per year of one tree species would be required to reduce overall forest biomass. Below this 10–25% range a decline in productivity of one or more species could be compensated for by increased productivity of one or more other species. It should be noted that while such compensations can occur in complex ecosystems they would not be present in agricultural monocultures.

Computer simulation exercises were performed to test some possible effects of acidic precipitation. The JABAWA computer model of forest growth was modified to include the effects of precipitation acidity on nitrogen availability and tree growth. The model found a direct positive relationship between N availability and biomass accumulation (1). The relationships between forest production, litterfall, and decomposition of litterfall were analyzed using the FORTNIT forest nitrogen model. The simulation model found that lower rates of litter decomposition would be compensated by higher forest floor biomass accumulation, so that N availability would not be greatly altered over a period of 15 to 40 years. After 40 years, slower rates of litter decomposition would (according to the model) provide higher N availiability due to the decomposition of the larger litterfall biomass. However, no field data are available to confirm these predictions (1). It seems obvious that only well-designed field experiments with an adequate amount of replication to overcome natural

variation will be needed to document alterations in natural ecosystems by acidic deposition, if present. Most published reports on altered forest productivity are subject to the criticism that other factors (biotic and abiotic) in the environment were not adequately controlled, documented, and/or accounted for. It is suggested that the use of moveable rainfall exclusion facilities on natural ecosystems may overcome the above criticism. Since variation in natural ecosystems may be greater than that in agricultural fields, as many as 10–20 plots per treatment may be necessary to detect statistically significant differences among treatments of less than 10%.

Overall Evaluation Effects of Precipitation Acidity to Terrestrial Vegetation

At the present time it appears that ambient levels of acidity in precipitation can have some deleterious effects on terrestrial vegetation. This statement is mostly derived from data on crops grown under field conditions. Experiments have been conducted under controlled-environmental conditions, but since plant responses to acidic rain grown under such conditions differ from responses under field conditions, data from controlled environments may only point to mechanisms. Few field experiments have been conducted that are statistically capable of detecting significant differences among treatments. Although decreases in yields of various crops have been documented in controlled-environment and field experiments at pH levels of pH 4.0 or below, only well-designed field experiments will document changes in plant productivity or survival that may be expected from actual acidic rainfall exposures. It is essential that experiments using standard agronomic practices or total ecosystem considerations with large numbers of replicates be conducted so results can be extrapolated to actual crop or ecosystem situations respectively. Large numbers of treatment replicates are needed to demonstrate differences (statistically significant) among treatments with means that differ by 10%.

In order to standardize results of future experiments, a uniform expression of data should be utilized. To date, the most meaningful relationships between rainfall acidity and plant responses have been obtained when responses are plotted as a function of the hydrogen ion concentration of the simulated rainfalls (30, 31, 33, 34). This expression or some other more meaningful expression should be used so data can be compared with ambient precipitation acidities.

Acidic precipitation may affect the productivity of crop and forest plants by direct or indirect means (necrosis or soil nutrient effects). If significant alterations in productivity of either crops or forest occur, significant financial impacts may result. Currently, evidence linking existing and/or anticipated levels of rainfall acidity to crop yield reductions is meager. From available data, it is clear that the amount of injury, if injury occurs, is less than

year-to-year changes in other abiotic and biotic factors. This does not mean, however, that possible injuries from acidic precipitation should be ignored. It is important to determine even small changes in productivity. Modeling exercises show that a growth reduction of 10–25% per year in one tree species would be required to reduce overall forest productivity. Below this 10–25% range a decline in productivity of one or more species could be compensated for by an increased productivity of one or more other species (11, 12). However, it should be noted that while such compensations may occur in complex ecosystems, they would not occur in agricultural systems. For example, a 1.0% reduction in yields of soybeans grown in the northeastern United States would represent a loss of 49.5 million dollars calculated for 1979 (ignoring price elasticity) (31, 33, 34).

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